CHEMICALLY ACTIVE AEROGELS FOR HOT GAS CLEAN-UP IN A IGCC PROCESS

Uschi M. Graham and Gerald Thomas. University of Kentucky, Center for Applied Energy Research, 2540 Research Park Drive, Lexington, KY 40511 - 8410.

Abstract

To aid the development of IGCC technologies, the unique properties of aerogels were exploited to research purifying systems for H_2S, NO_x and Hg that are durable and efficient. Aerogels can be used to capture hot gases based on their high surface areas and great tendency to form composites with various other sorbents or structural supports. Silica aerogels are at the heart of the study. Sol-gel synthesis achieved chemically active silica aerogels which were used as structural supports for diverse catalysts depending on the type of gases. Carbon aerogels are also included, focusing mainly on H_2S (g) sorption. Varying the nano- and microstructure of the aerogels and supported metal catalysts further aids in the hydrogenation of CO_2 and selective catalytic reduction of NO_x. Among the sol-gel composite materials applied in this study, those being composed of both organic and inorganic components (organic-inorganic hybrid composites) are observed to have particularly strong affinities for mercury thereby achieving an effective mercury control.

Keywords: aerogels, micro-structure, adsorption

Introduction

Today, coal supplies more than 55% of the electricity consumed in the United States, and it is likely to remain the dominant source of fuel for electric-power generation well into the next century. Integrated gasification-combined-cycle (IGCC) technology is one of the most promising new prospects for electricity from coal to emerge in recent years. It is one of the cleanest methods of generating coal-fired electricity. Rather than burning coal directly, the IGCC technology begins by converting the coal into a combustible gas. The gas itself can be stripped off its impurities, a process capable of reducing about 95% of the sulfur in coal. In addition the technique removes about 90% of the nitrogen oxide pollutants. Because of the IGCC's higher efficiencies in producing electricity compared with conventional coal power plants, a given amount of fuel will produce correspondingly less greenhouse gas leading to a reduction of carbon dioxide gas by at least 35%. However, the gasified coal also contains sizable quantities of hydrogen sulfide (H_2S), a rather toxic gas that also has undesirable corrosive effects on the pipes and turbines. Various sulfidation mechanisms have been suggested during the absorption of $H_2S(g)$ by bulk sorbents, or by a novel concept involving the conversion of $H_2S(g)$ to $H_2(g)$ and elemental sulfur by applying electrochemical membranes. [1]

Previous studies demonstrated different ways of cleaning the acid gas emissions prior to burning in a combustion turbine, including SO_2, NO_x and CO_2 by converting them into marketable commodities including sulfur, sulfuric acid, gypsum and fertilizers.[2] Although the bulk of the pollutants can be effectively controlled, there is still much uncertainty over the technically most effective approach for controlling mercury emissions and also on how to capture those small amounts of residual $H_2S(g)$ which escaped from the primary recovery phase.

The dominant source of anthropogenic mercury emissions in the United States is derived from coal since conventional particulate control devices can not capture mercury in either of its gaseous forms (Hg^0; $Hg^{2+}X$) effectively. The Environmental Protection Agency (EPA) estimated that mercury from power plants accounts for 45 % of the total 158 tons/yr.[3] During coal gasification mercury is completely volatilized and a promising approach for mercury control is the injection of an effective sorbent. New IGCC technologies need to address an effective mercury control and previously obtained data for mercury sorbent developments designed for coal fired boilers provide a vast source of information. [4-5] Recent findings [ss] indicated a poor sorbent performance of mercury on activated carbon substrates in the presence of the acid gases SO_2, HCl, NO, and NO_2, a typical gas mixture always to be expected during gasification of coal. The interaction of SO_2 and NO_2 was observed to be particularly detrimental on the sorbent performance. For example NO_2 in a simulated flue gas inhibits $Hg^0(g)$ adsorption on activated carbon but promotes the formation of $Hg^{2+}X$ (e.g., X corresponds to $Cl_2(g)$ or $O(g)$; mercuric solids are possible in the presence of sulfate and sulfide) instead which occurs at $NO_2(g)$ concentrations as low as 20 ppmv [7]. Although the mechanisms of the mercury-sorbent-interaction in the presence of SO_2 and NO_2 are not understood it is known that the $Hg^0(g)$ typically is converted to a volatile oxidized form and it is suggested that the sorbent's oxidized surfaces catalyze the reaction. [8-9] Since the IGCC technology helps eliminate fly ash emissions completely, the interactions between $Hg^{2+}X$ and fly ash particle surfaces and, hence, any respective surface-catalytic effects typically occurring during flue-gas/fly ash interactions can be neglected for the purpose of this investigation. Experimental results from the sorbent-mercury-flue gas interactions may be extrapolated to the IGCC system.

In the case of mercury, carbon sorbents have been used with varying success because of the interfering reactions mentioned earlier. However, in case of $H_2S(g)$, carbon sorbents offer excellent recovery potential from the hot flue-gas stream even under a wide range of different operating conditions. It has also been suggested that the carbons may be used as an active support for either copper or zinc oxides to further enhance the sorption process. [10] Instead of injecting activated carbon as a sorbent in a IGCC system this study focuses on the unique properties of advanced aerogel materials.

Objectives

Experiments are performed to capture both mercury and hydrogen sulfide, but not necessarily on the same aerogels. The overall objective is to identify conditions for effective capture using chemically active aerogels (and aerogel composites). Applications for aerogel materials include additives for advanced composite materials, such as more reactive sorbents. It is the study's primary objective to observe the affinity of chemically enhanced aerogels towards capturing gaseous mercury species even in the presence of a typical flue gas mixture including NO_2 and SO_2. Another approach focuses on scrubbing dilute quantities of $H_2S(g)$.

Materials

Aerogels are highly porous, semi-transparent metal oxide materials. [11-12] They are very light (the lightest have a density of only 3 times that of air, i.e. 0.003 g/cm^3) and are characterized by excellent heat resistance (up to 800 °C), an important property allowing us to use aerogels to clean hot flue gas emissions. They have extremely high surface areas (600-1000 $m^2/_g$) and are the product of supercritical drying of a sol-gel produced alcogel. [13, 14, 15] The combination of their properties makes them attractive for a number of reasons to be used in the adsorption and safe storage of pollutants from IGCC processes.

A thorough review of the sol-gel process used in this study, describing the transition of a system from liquid, mostly colloidal, into a solid gel phase can be found elsewhere. [16-17] In general, the sol-gel chemistry is based on the hydrolysis and condensation of metal alkoxides $M(OR)z$. These reactions can be generalized as follows:

MOR + H_2O → MOH + ROH [hydrolysis]
MOH + ROM → M-O-M + ROH [condensation]
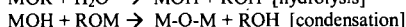
The silica aerogel pore network can be characterized by an open-pore structure. The flue gas can flow from pore to pore, and eventually through the entire aerogel. It is this property that makes aerogels effective sorbents for gas phase infiltration and reaction. Although the silica aerogels possess pores in the micro, meso, and macro size range, the majority of the pores fall in the mesopore regime (diameters between 2-50 nm). The carbon aerogel also has predominantly meso pores with a slightly larger pore radius and pore sizes >100 nm. The pore size distribution of the silica and carbon aerogels used in this study are shown in Figure 1.
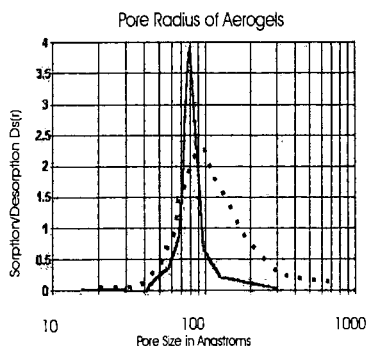

Figure 1 illustrates the distribution of pore radius for a silica aerogel (solid curve) and for a carbon aerogel (dotted curve).

Carbon aerogels are composed of covalently bonded, nanometer-sized particles that are arranged in a 3-dimensional network. Unlike conventional carbon blacks that are produced from gas phase reactions,

these materials are derived from the sol-gel polymerization of selected organic monomers in solution. After the solvent was removed, the resultant organic aerogel was pyrolyzed in an inert atmosphere at 600 °C from 45 minutes to form a carbon aerogel. This material has high porosity (>50%) due to pores that are less than 100 nm in diameter (see Figure 1). Unlike activated carbon powders, the carbon aerogels have high surface areas (ranging from 400-1000 $m^2/_g$) which are inherent to the sol-gel process and do not depend on "activation" procedures. A characterization of the primary particles that make up the aerogel network shows that they are composed of nanocrystalline, graphite-like ribbons that are intertwined to form the particles. Another very important distinction from other high surface area carbon powders is that carbon aerogels have oxygen free surfaces that can increase their effectiveness in some applications, particularly in the presence of NO_2 and SO_2 in a typical hot flue gas mixture. The gas/vapor adsorption method was used for determining this study's aerogel surface areas (silica aerogel: 980 m^2/g and carbon aerogel: 750 $m^2/_g$).

Sample Preparation:

Aerogels are ideal for use in composites where the silica aerogel makes up the substrate and additional phases are added during sol-gel processing. This study used three different kinds of added materials into the silica sol-gel. The first test included spheres of preformed carbon aerogels. The second test involved a porous activated carbon (NORIT) and the third test uses a reducing gas to modify the aerogel composites formed in tests one and two. This procedure allows fabrication of chemically altered aerogel materials that also retain their structural integrity. The aerogel materials produced using this technique typically exhibit a variety of unique properties, such as enhanced chemical activity.

Experimental Setup and Discussion of Results

Mercury adsorption test on aerogels:

Mercury in a flue-gas stream is present only in trace quantities (5-12 $\mu g/m^3$) and this study focused on using 10 $\mu g/m^3$ at the inlet valve. The aerogel material was finely distributed on a silica filter and packed in a quartz-glass reactor (both have negligible surface areas compared with the aerogel). A mercury analyzer (Semtech 2000) was utilized to measure Hg^0 (g) on a continuous basis for up to three hours. The proportions of the different species, Hg^0(g) and $Hg^{2+}X$(g) in the IGCC system are not understood and, therefore, the experiments were repeated and total mercury at the outlet was monitored after passing the exiting gas over a $SnCl_2$ reducing unit (as was done successfully in related mercury studies [6-7]). Sorbent mass (for different aerogels) was set to range between 10-100 mg which is well beyond the range where mass transfer might be of concern, however, the pure aerogels have extremely low densities while the composites (aerogel plus active carbon) assume greater densities depending on the carbon loading ratios. A significant sorbent/mercury mass ratio of at least 1000/1 requires a minimum of 10 mg/m^3 of sorbent. The transport of mercury species to the aerogel's active surface sites was facilitated using a typical flue gas mixture (Table 1) containing ~ 7 % H_2O vapor. Due to the elevated temperatures of the experiments (120-250 °C) the aerogels will not absorb any moisture. As the samples cool, however, the surfaces, which are covered with hydroxyl groups (~ 5 -OH/nm^2) tend to exert strong hydrogen-bonding effects, causing the surfaces to act hygroscopic and handling procedures become more difficult. Although the aerogels's tendency to attract water can be eliminated through simple treatment with trimethylsilyl /or other non-polar aliphatic groups (-OR), this study preferred the presence of the polar acidic counter parts for the inorganic fraction of the aerogel composites.

Results of the mercury adsorption onto different aerogels are summarized in Table 2. In general, after a maximum of three hours of exposure time of the simulated hot flue gas (see flue-gas; Table 1), the chemically active silica aerogel (AERO-I), which had been pretreated with a reducing gas (H_2), adsorbed 92 % of the total mercury (58 % after 30 minutes exposure). The aerogel composite utilizing the NORIT activated carbon product (AERO-II) adsorbed 43 % of the total mercury after 3 hours and less than a third of that amount after 30 minutes. Without the $SnCl_2$ reducing unit, only 17 % of Hg^0(g) was detected after the maximum exposure time suggesting that the majority of the mercury was oxidized by the sorbent interaction. Without chemically activating the silica aerogel, the active carbon/aerogel composite functioned predominantly as a catalytic surface to oxidize the Hg^0(g) (even without the presence of chlorine species to form the thermodynamically most stable form of $Hg^{2+}X$(g)), but did not have excellent sorption capacity for the mercury as did the AERO-I. The third aerogel utilized in this study (AERO-III), which was also prepared as a composite, but incorporated a carbon aerogel rather than the activated NORIT, had good sorption capacity towards mercury, adsorbing 71 % of the total inlet mercury concentration after 3 hours (54 % after 30 min.). However, the overall capacity was somewhat less compared with the chemically active silica aerogel (AERO-I). This study suggests that the difference in oxygen concentration on the surfaces of the NORIT carbon and carbon aerogel may significantly influence the conversion reaction of Hg^0(g) to $Hg^{2+}X$(g) and the dominant species for chemisorption seems to be Hg^0.

Table 1 Flue-gas used in Hg tests

Carrier Flue Gas	% vol
H_2O	7
SO2	1000ppm
NO2/NO	1000ppm
N2	Difference
CO2	12
O2	6
Hg	$(10 \ \mu g/m^3)$

Table 2 Results for Hg adsorption on aerogels*

Sorbent Type	Hg adsorption 30 min	180 min
AERO-I	58 %	92 %
AERO-II	11 %	43 %
AERO-III	71 %	54 %

* Table 2 shows mercury adsorption expressed as percent of the total Hg removed from the system after exposure time.

$H_2S(g)$ adsorption tests on aerogels

The combination of in-situ desulfurization (50-60% desulfurization degree) and external desulfurization (completion until >90% sulfur capture) offers an attractive practical solution for hot sulfur abatement in IGCC systems. Work on the use of injected sorbents for in-situ gas desulfurization showed that for sorbent particles injected at high temperatures (1650°C), CaO for example preferably reacts with the silicate phase typically present in coal slag instead of the H_2S present in the gas phase. Besides carbon based sorbents, various metal oxide sorbents, either ZnO-based or CuO-based, as well as mixed metal oxides (binary and tertiary combinations) have been compared in previous works. [10] In this study the H_2S was carried to the aerogel sorbent using a carrier gas (Table 3) that had a composition similar to that typically present in a IGCC system after the majority of sulfur had already been pre-scrubbed (recovered as value-added products). The simulated gas was enriched with 1000 ppm H_2S for the tests and the temperatures of the runs were fixed at 800 ° C. Results are summarized in Table 4.

Table 3 Carrier gas for H_2S

Carrier gas	%vol
H2	30.5
CO	39.5
CO2	10.8 1
H2S	1000ppm
N2	Difference
H2O	1.5
T °C	800 °C

Table 4 Results for H_2S adsorption on aerogels

Sorbent type	H_2S adsorption
AERO-1	NA
AERO-II	complete after 1 h
AERO-III	complete after 10 min.

The chemically activated silica aerogel (AERO-1) was not used for the $H_2S(g)$ adsorption tests. The aerogel composite with the NORIT carbon (AERO-II) had excellent adsorption capacity with all of the $H_2S(g)$ being captured after 1 hour exposure time. The carbon aerogel-composite (AERO-III) had much faster reaction rates compared with the NORIT carbon and complete $H_2S(g)$ capture was observed after only 10 minutes exposure time. Although both kinds of sorbents have excellent capacities, the mechanisms that control capture in the case of the carbon aerogel (AERO-III) are superior due to the rapid kinetics. To better understand the sorbent performance, experiments are required to further determine sorption rates as a function of reactor conditions.

The final experiment involved both mercury and $H_2S(g)$. The AERO-III that was first used to chemisorb $H_2S(g)$ was cooled to 200 ° C and then a flue-gas enriched in 10 $\mu g/m^3$ mercury was passed over the sorbent. The H_2S molecules which had chemisorbed onto the aerogel composite (this study was not able to tell whether the H_2S molecules attached to the silica surfaces, or to the carbon surfaces, or both) reacted with the mercury to form HgS crystallites which can be seen in a high resolution SEM shown in Figure 2.
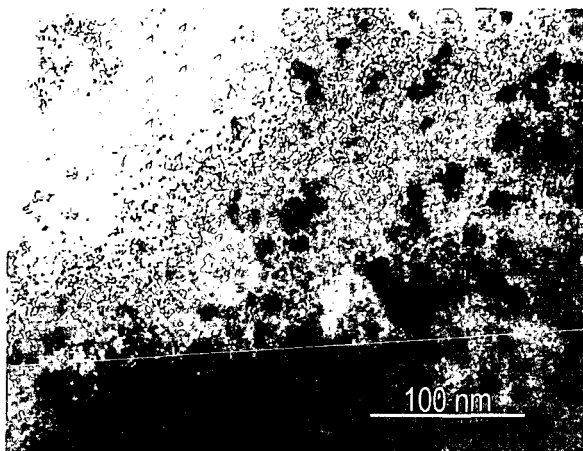
Figure 2 illustrates a high resolution SEM of the aerogel composite AERO-III after adsorption cycles involving first H₂S sorption at 800 ° C and, after cooling to 200 ° C, a second adsorption cycle with a typical flue gas enriched in mercury was performed. The dark circles represent sites where HgS nucleated and grew within the composite AERO-III.

Synopsis

Ideally, new IGCC technologies provide electricity while conforming to the strictest air-quality requirements and there is a driving force to find new and enhanced sorbents. Aerogel composites through sol-gel processing including silica and carbon based aerogels were shown to have excellent potential to adsorb both mercury and $H_2S(g)$ and future experimental work needs to focus on optimizing the conditions at which these sorbents could become economically feasible.

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